

Super hydrophobic coated substrates

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Field of the invention

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The present invention relates to super hydrophobic coated substrates having a static water contact angle of more than 120°.

Background of the invention

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For instance, U.S. Pat. No. 3,498,527 teaches that paper board containers for liquids can be waterproofed by application of a waterproofing coating such as wax or polyethylene, and a similar method is shown in U.S. Pat. No. 2,708,645 for waterproofing paper drinking cups and in U.S. Pat. No. 3,212,697 for paper grocery sacks. In U.S. Pat. No. 3,597,313, temporary wet strength is imparted to paper by coating it with a polymeric alcohol-polymeric aldehyde reaction product.

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Coating processes, by themselves, have been used to produce disposable articles of sanitary clothing. In U.S. Pat. No. 3,078,849, a disposable sanitary napkin is disclosed which consists of an adsorbent layer having a liquid-repellent backing of polyvinyl alcohol or similar material capable of initially repelling water but eventually solubilizing. The degree of water-repellency, therefore the lifetime of the napkin, is controlled by varying the thickness of the backing. Because the

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necessary life of the napkin cannot be predicted by manufacturer or user, the backing must be sufficiently thick to take account of all normal contingencies. U.S. Pat. No. 3,542,028 is directed to a flushable sanitary napkin consisting of a cellulosic sheet treated with a fluoropolymer coating. U.S. Pat. No. 3,559,650 teaches the preparation of a sanitary napkin having two flush-disposable sides separated by a waterproof film too thin to support itself once both faces of the napkin have disintegrated upon disposal.

Analogous to the process of coating a surface with a waterproofing substance is the concept of reacting a surface with another material so as to form a reaction product on the surface which has water-repellent properties. For example, U.S. Pat. Nos. 2,130,212 and 3,137,540 teach that materials such as polymeric alcohols may be reacted with other materials to increase their water-repellent properties. The latter patent teaches treating polyvinyl alcohol articles with an aqueous emulsion of an aldehyde to impart water-repellency thereto. U.S. Pat. No. 3,626,943 teaches that disposable diapers can be made from polyvinyl alcohol and waterproofed on one side by reaction with formaldehyde. These reaction-type coating processes suffer from drawbacks. They are carried out in the aqueous phase which is complicated and requires relatively large quantities of reagents. Most of the processes which employ some form of in situ chemical reaction to produce a water-repellent surface are carried out in the liquid phase, some vapor phase treatments are taught by U.S. Pat. Nos. 2,306,222; 2,961,388; and 3,017,290.

A known method of water and oil repellent finishing of textiles, described in USSR Patent 1,158,634, includes plasma treatment in a glow discharge in an atmosphere of inorganic gases, followed by treatment with a fluorine containing acrylic monomer in gas phase. Another prior method of achieving film plasma polymerization, described in U.S. Pat. No. 4,188,426, includes treatment in a glow discharge of per-fluoro-cyclo-butane or hexafluoroethane to reduce the friction coefficient and to improve the surface hydrophobia of organic and

inorganic substrates (e.g. polyethylene films, metals). However these disclosures do not achieve a level of water repellency as the present invention.

Plasma-deposited fluorocarbon coatings are often cited in the literature as "teflon-like coatings" because their CF_x ($0 < x \leq 2$) composition and surface energy can be made very close to that of polytetrafluoroethylene (PTFE, $-(\text{CF}_2-\text{CF}_2)_n$), known on the market as Teflon®.

Plasma coating processes of metals, polymers, and other substrates, with fluorocarbon films are known in the art. As an example, it is known from USP 4 869 922 and from other sources, that deposition from continuous (i.e. non modulated) radiofrequency (RF) glow discharges fed with fluorocarbons provides films, layers, tapes, plates, and differently shaped articles made of plastics, metals or other materials, with a thin fluorocarbon coating, with no other material interposed between the coating itself and the substrate. Such coatings are claimed to have very good adherence to the items processed, to be void-free, to be uniform or not porous, and to show controlled wettability characteristics, which depend on their surface chemical composition. The non modulated, continuous plasma process of the above mentioned patent leads to coatings characterized by static water contact angle (WCA) values lower than 120° .

Glow discharges treatments are also considered in US-A-5 462 781 for improving the bondability of an implantable polymer medical device or for changing the wettability of a polymer fabric. Several of the references discussed in this patent confirm non modulated, continuous plasma treatments as a means for varying the inherent WCA of a surface.

US-A-5 034 265 discloses a non modulated, continuous plasma treatment for improving the biocompatibility of vascular grafts with a CF_x fluorocarbon coating deposited at the inside wall of the grafts in a proper plasma reactor fed with tetrafluoroethylene (C_2F_4 , TFE) at 0.2 Torr. In the preferred embodiment of the

invention no other materials are interposed between the substrate and the coating.

U.S. Pat No 5,328,576 discloses a method for imparting water and oil repellent surface properties to fabrics or paper that includes pretreatment in a low pressure oxygen plasma in the presence of water vapor followed by plasma polymerization of methane in a high frequency glow discharge carried out in the same treatment chamber. This method doesn't deliver durable, permanent coatings with a WCA higher than about 120°.

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U.S. Pat. No. 5,262,208 discloses an gas plasma treatment for archival preservation of paper manuscripts by a thin film protective polymer film. The treatment time is ranging from 30-3600 seconds. Other methods have been used to obtain thin coatings on the web materials with short treatment periods. Providing surface treatment is disclosed in US Patent No. 4,842,893 and 4,954,371 which describe a process for high speed coating of substrates with a complete and uniformly adhering layer and using electron beam radiation curing of the vapor deposited monomers for multilayer capacitors. U.S. Pat. No. 4,842,893 discloses high speed coating process including flash vaporization system and electron beam curing. Both of these electron beam disclosures are incorporated herein by reference. Other uses of electron beam coatings in the electronic industry field have been reported by Westinghouse science & technology center USA (Adv. Mat. Newsletter Volume 13, No 9, 1991 page 4).

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Summary of the invention

Specifically, the present invention, having the features mentioned in the annexed claims, relates to substrates coated with a thin, well adherent, nonporous, fluorocarbon coating with super hydrophobic properties, i.e. characterized by static water contact angle (WCA) values, measured on a smooth and plane surface, higher than about 120°, preferably higher than 130°, more preferably higher than 150°. Substrates treated with this method have their hydrophobicity markedly

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improved, e.g. can be made effectively waterproof while maintaining their previous characteristics such as permeability to gases and vapors. The increased hydrophobicity results also in additional benefits such as prevention of build-up of soiling (e.g. on hard surfaces such as glass, ceramics, metals and other surfaces exposed to dirt), prevention of lumping of powders or granules, aiding in complete emptying of containers which contain hydrophilic materials such as liquid detergent or shampoo bottles or beverage containers or liquid tanks or flowable particle tanks e.g. flour tanks, prevention of contamination and build-up on toothbrushes and bristles. If the substrates are polymeric, they can be useful e.g. in making breathable products with improved resistance to leakage of body fluids.

The present invention deals with treated polymeric or non polymeric articles whose surface is made super hydrophobic, i.e. characterized by static water contact angle (WCA) values higher than about 120°, preferably higher than 130°, more preferably higher than 150°.

The substrates of interest for the present invention may include a wide range of materials in form of webs, tapes, films, powders, granules, particles, woven and non-woven layers; substrates can be porous or non-porous, molded or shaped, rigid or flexible, made of polymers, textiles, papers, cellulose derivatives, biodegradable materials, metals, ceramics, semiconductors, and other inorganic or organic materials. Preferably, the substrate is formed into a desired shape or configuration, depending on its intended use, before being subjected to the treatment object of this invention.

When organic synthetic resins are chosen, such substrate materials could be fabricated from polyethylene, polyacrylics, polypropylene, polyvinyl chloride, polyamides, polystyrene, polyurethanes, polyfluorocarbons, polyesters, silicone rubber, hydrocarbon rubbers, polycarbonates and other synthetic polymers.

The articles are preferably subjected to a modulated glow discharge plasma treatment performed with a fluorocarbon gas or vapor compound fed in a prop-

erly configured reactor vessel where the substrates are positioned. The plasma process deposits a continuous, fluorocarbon thin film with super hydrophobic surface characteristics, tightly bound to the substrate.

- 5 Alternatively a more conventional thin film coating process followed by high energy surface curing can be used. This is the method of using a high speed vacuum coating process for producing durable and thin water-repellent coatings on a substrate. It uses e.g. a movable support such as rotating drum in a vacuum chamber. The surface of the support is maintained at a temperature sufficient to
10 permit condensation of a vaporized material deposited in the chamber. The material is a curable monomer with a relatively low molecular weight. The monomer vapor is created using a flash vaporizer. The desired amount of curable monomer is metered to a heated flash vaporizer system where the material is vaporized. It is then transported e.g. by it's inherent pressure, to the
15 substrate resting on the rotating drum and condensed on the surface of the substrate. According to the method the substrate is then transported to a curing means such as an energy source which emits an electron beam, UV-light radiation or exposure to an electro magnetic field. Alternative the curable monomer can also be transferred into radicals by passing through a plasma zone
20 (zone of high voltage discharge). The curing of the monomer by the curing means then provides a coating on the substrate surface which has a static water contact angle of more than 95°.

- The method for delivering the curable monomer to the substrate for minimizing
25 the amount of monomers can use an ultrasonic atomizer producing micro droplets of curable monomer. They are released into a vaporization tube heated by band heaters. The atomized droplets impinge on the inner wall of the vaporization tube and are instantaneously vaporized, i.e., flash vaporized. This reduces the opportunity for polymerization prior to being deposited on the
30 substrate.

In one aspect of the present invention, the substrate can be one side water-repellent and capable of absorbing and storing fluids from the other side, or alternatively be repellent on both sides.

5 "Plasma," as used herein, is used in the sense of "low-temperature plasma" or "cold plasma" produced by igniting a glow discharge in a low pressure gas through a power supply. Glow discharges contain a variety of species chemically active and energetic enough to cause chemical reactions with surfaces exposed, i.e. covalent bonding to a suitable substrate material. Cold plasmas, or glow dis-
10 charges, are generally produced with high frequency (from KHz to MHz and GHz) power supply (HF plasmas). Electrons, positive and negative ions, atoms, excited molecules, free radicals, and photons of various energies are formed in a cold plasma.

15 "Modulated plasma" means a non continuous plasma, HF plasma, i.e. a glow discharge whose driving power is pulsed between a maximum value and zero (ON/OFF pulse) or a fraction of it, at a certain frequency, with a proper pulse generator connected to the main power supply. In the case of ON/OFF pulsed systems, the time ON and time OFF values are among the experimental pa-
20 rameters of the process. Superimposing a triggering ON/OFF pulse to the main high frequency field which generally drives a glow discharge, alternates short continuous discharges with plasma OFF time intervals where active species still exists in the gas phase, but the effects of ions and electrons are strongly re-
25 duced. This alternating exposure to two different processes leads to unique surface modifications of substrates, which are very different from those of continuous plasma process, as it will be shown.

"Plasma deposition" or "plasma polymerization" is the plasma process that leads to the formation of thin (0.01 - 2 μm), partly crosslinked, void-free, continuous
30 coatings well adherent to substrates. The molecules of the gas phase are fragmented by energetic electrons, which are able to break chemical bonds; this process leads to radicals and other chemical species which are able to deposit at

surfaces inside the vacuum chamber and form a thin, uniform film. The action of the plasma may also affect the surface of a polymer substrate in the early deposition time; energetic species may break bonds in the substrate with possible evolution of gas products, such as hydrogen, and formation of free radical sites which contribute to form covalent bonds between the growing film and the substrate.

Substrate to be treated are subjected to modulated plasma gas discharge in the presence of at least one fluorocarbon gas or vapor. Specifically, fluorocarbon gases or vapors such as tetrafluoroethylene (TFE, C_2F_4), hexafluoropropene (HFP, C_3F_6), perfluoro-(2-trifluoromethyl-)pentene, perfluoro-(2-methylpent-2-ene) or its trimer may be used, TFE being the presently preferred choice. The plasma deposition process is preferably performed by positioning the substrate in a properly arranged plasma reactor, connecting the reactor to a source of a fluorocarbon gas or vapor, regulating flow and pressure of the gas inside the reactor, and sustaining a glow discharge in the reactor with a high frequency electric field in a pulsed (modulated) mode by means of a suitable pulsed power supply. The parameters which define the glow discharge treatment includes the feed gas or vapor, its flow rate, its pressure, the position of the substrate inside the reactor, the design of the reactor, the exciting frequency of the power supply, the input power, the time ON and the time OFF of the pulsing system. Substrates, as those listed in the abstract, may be positioned in the "glow" region of the discharge, i.e. directly exposed to the plasma, or in the "afterglow" region, i.e. downstream respect to the visible glow. The two positions generally result in coatings with different composition and properties; treating the substrates with modulated glow discharge results also in different coatings respect to continuous treatments.

It has been found that it is possible to deposit thin fluorocarbon films with super hydrophobic characteristics, i.e. showing a surprisingly high WCA value, even up to about 165° . The present invention thus provides substrates of the type mentioned above, with fluorocarbon films characterized by a WCA value higher than

120°, preferably higher than 130°, more preferably higher than 150°.

According to the present invention, fluorocarbon coatings with F/C ratio from about 1.50 to about 2.00 have been deposited, characterized by WCA values higher than about 120°, such as between about 155° and about 165°. The coatings have been deposited at the surface of different polymer and non polymer substrates such as polyethylene (PE), polypropylene (PP) polyethyleneterephthalate (PET), and paper in form of films and fabrics, glass and silicon, among many. It should be noted that the F/C ratio could be theoretically up to 3, if the coating would be formed only by a mono-molecular layer of CF₃ groups. But the formation of intermolecular cross-links and the formation of claims (containing CF₂ fragments) which are grafted onto the surface lowers the above theoretical value so that the obtained coatings, notwithstanding the fact that they contain many CF₃ groups, have a global F/C ratio in the range of about 1.50 to about 2.00.

The thickness of the coatings depends on the duration of the plasma process at different conditions, and can be kept between 0.01 and 2 µm. It has been found that the nature of the substrate materials does not influence neither the chemical composition nor the thickness of the coatings. Coatings with WCA values up to about 165° (e.g. 165° ± 5°) were obtained.

Brief description of the drawings

In the following detailed description the invention will be described, purely by way of example, with reference to the enclosed figures of drawing, wherein:

- Figure 1 compares a conventional "continuous" RF glow discharge with an ON/OFF "modulated" RF glow discharge;
- Figure 2 portrays a typical scheme of a plasma reactor adapted for use within the context of the invention;
- Figure 3 shows a C1s ESCA signal of an uncoated polyethylene substrate wherein the signal is due only to C-H, C-C bonds of the substrate;

- Figure 4 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (glow position, continuous mode), with WCA of $100 \pm 5^\circ$; the signal is composed by components due to CF₃, CF₂, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination;

- Figure 5 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (afterglow position, continuous mode), with WCA of $120 \pm 5^\circ$; the signal is composed by components due to CF₃, CF₂, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination; and

- Figure 6 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (glow position, modulated mode), with WCA of $165 \pm 5^\circ$; the signal is composed by components due to CF₃, CF₂, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination.

Detailed description of the invention

Figure 1 compares a conventional "continuous" plasma (figure 1a) with the modulated process of the invention, (figure 1b) showing pulsed alternating plasma ON with plasma OFF (i.e. no plasma) times. The two processes are schematized by referring to their driving signals.

The reactor 1 schematically shown in figure 2 was utilized not exclusively for developing the deposition method object of the present invention. The reactor vacuum chamber 1 is made of Pyrex glass, is provided with an external RF powered electrode 2 and an internal grounded electrode 3. The external electrode is connected to a power supply 4 (typically a radiofrequency generator operating at e.g. 13.56 MHz) through a matching network and an ON/OFF pulse generator 5. The substrates can be treated in the "glow" region of the reactor, onto the grounded electrode 3, as well as in its "afterglow" position i.e. at an afterglow substrate holder 6. The gas/vapor is fed through a proper mass flowmeter through a

gas/vapor feeding manifold 7, and its pressure, measured at the pump out exit 8 of the reactor, kept at a certain constant value with a manual valve on the vacuum connection between the reactor and its pumping unit. Even though the arrangement shown in the drawing represents a presently preferred choice, those skilled in the art will immediately recognize that pulsed energization of the plasma reactor can be achieved by different means such as direct energization by means of pulsed RF generators commonly used in radar and telecommunication techniques.

10 Preferably, the deposition process is performed with an RF (13.56 MHz) generator. The RF power delivered to the external electrode of the reactor is kept in the 1-500 Watts range for a power density of 0.02-10 Watt/cm². The reactor is fed with a fluorocarbon compound at a 1-100 sccm flow rate and is kept at a constant pressure of 50-1000 mTorr during the process. Preferably, the glow discharges are modulated through the pulse generator, preferably at 1-500 ms time ON and 1-1000 ms time OFF values, with respective values of about 10 ms and about 190 ms being the most preferred choice at present. The deposition process may range from a few seconds to many hours; during this time a uniform fluorocarbon coating is deposited on the substrates positioned in the glow as well as on those in the afterglow region. The deposition rate, a typical one being in the 20 - 400 Å/min range, was measured by weighing (weight/time) the substrates before and after the discharge, or by measuring the thickness of the coatings (thickness/time) with an Alpha Step profilometer. The deposition rate and the chemical composition of the coating depend on the experimental conditions (pressure, power, substrate position time ON, time OFF, gas feed and flow rate) of the discharge.

The coatings obtained are uniform over the entire surface of the substrate; when deposited on flat (i.e. plane), smooth substrates, their hydrophobic character has been estimated through their static WCA value, as measured with a WCA goniometer. The measurement is done on a flat, i.e. plane, and smooth surface of a substrate after coating. The term smooth as used herein for water contact angle

measurements refers to a roughness of no more than 5 microns in accordance with standard roughness measurements on continuous surfaces. WCA values in the range about 120° to about 165°, corresponding to a critical surface tension lower than that of PTFE (18 dynes/cm) have been measured for fluorocarbon CF_x coatings, when x ranges between about 1.50 and about 2.00. The chemical composition of coatings is preferably determined by Electron Spectroscopy for Chemical Analysis (ESCA) within the sampling depth of the technique (about 100 Å). The adherence of the coating to the substrate is very good.

The following examples are given for the purpose of still better illustrating the inventive concept of the present invention, and for highlighting the advantages of using modulated over continuous treatments.

EXAMPLE 1

Three sets of substrates of silicon, PE and PP, of areas in the range of 2-10 cm² per substrate, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. A similar set of substrates was positioned in the after-glow position at 6. C₂F₄ was set to feed continuously the reactor at 6 sccm, and the pressure set at 300 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge with 50 Watt of input power for 90 min, then switched off.

Another glow discharge was subsequently run with a similar set of substrates positioned in the glow position and no substrates in the afterglow position, under the same conditions described above except for the fact that modulation was effected at 10 ms time ON and 190 ms time OFF through the pulse generator.

At the end of the two discharges the substrates were extracted from the reactor and their WCA measured. The WCA values shown in Table 1 were found, which are compared to the WCA values of the unprocessed substrates. A deposition rate of 30 ± 5 Å/min was measured for the coatings deposited in the modulated

mode.

Other substrates, treated in the two modes, were analysed with the ESCA technique. Their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Tables 2a-c. No other elements were detected (e.g. Si for silicon substrates), which means that the coatings are continuous. The C1s spectrum of the uncoated PE substrate is shown in Figure 3, while the C1s spectra of PE samples coated as described above are shown in Figures 4, 5 and 6, respectively.

Table 1

SUBSTRATE	Si	PE	PP
WCA unprocessed	$15^{\circ} \pm 3^{\circ}$	$95^{\circ} \pm 3^{\circ}$	$85^{\circ} \pm 3^{\circ}$
WCA continuous discharge (glow position)	$100^{\circ} \pm 5^{\circ}$	$100^{\circ} \pm 5^{\circ}$	$100^{\circ} \pm 5^{\circ}$
WCA continuous discharge (afterglow position)	$120^{\circ} \pm 5^{\circ}$	$120^{\circ} \pm 5^{\circ}$	$120^{\circ} \pm 5^{\circ}$
WCA modulated discharge (glow position)	$165^{\circ} \pm 5^{\circ}$	$165^{\circ} \pm 5^{\circ}$	$165^{\circ} \pm 5^{\circ}$

Table 2a

ESCA results for the continuous discharge (glow position) of Example 1

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	43.3	42.4	42.9
fluorine atomic %	56.7	57.6	57.1
F/C ratio	1.31	1.36	1.33

Table 2b

ESCA results for the continuous discharge (afterglow position) of Example 1

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	34.4	33.8	34.1
fluorine atomic %	65.6	66.2	65.9
F/C ratio	1.91	1.96	1.93

Table 2c

ESCA results for the modulated discharge (glow position) of Example 1

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COATED SUBSTRATE	Si	PE	PP
carbon atomic %	36.4	36.2	36.7
fluorine atomic %	63.6	63.8	63.3
F/C ratio	1.75	1.76	1.72

EXAMPLE 2

Three sets of substrates of glass, silicon and PE, of areas in the range of 2-10 cm² per substrate, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. A similar set of substrates was positioned in the after-glow position. C₃F₆ was set to feed continuously the reactor at 5 sccm, and the pressure set at 300 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge with 50 Watt of input power for 60 min, then switched off.

Another glow discharge was subsequently run with a similar set of substrates positioned in the glow position and no substrates in the afterglow, under the same conditions described above except for the fact that modulation was effected at 10 ms time ON and 90 ms time OFF through the pulse generator.

At the end of the two discharges the substrates were extracted from the reactor and their WCA measured. The WCA values shown in Table 3 were found, which

are compared to the WCA values of the unprocessed substrates. A deposition rate of $70 \pm 5 \text{ \AA/min}$ was measured for the coatings deposited in the modulated mode.

- 5 Other substrates, treated in the two modes, were analysed with the ESCA technique; their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Tables 4a-c. Also for this case, since no other elements were detected (e.g. Si for silicon and glass substrates), the coatings were assumed to be continuous.

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Table 3

SUBSTRATE	glass	Si	PE
WCA unprocessed	$35^\circ \pm 3^\circ$	$15^\circ \pm 3^\circ$	$95^\circ \pm 3^\circ$
WCA continuous discharge (glow position)	$105^\circ \pm 5^\circ$	$105^\circ \pm 5^\circ$	$105^\circ \pm 5^\circ$
WCA continuous discharge (afterglow position)	$120^\circ \pm 5^\circ$	$120^\circ \pm 5^\circ$	$120^\circ \pm 5^\circ$
WCA modulated discharge (glow position)	$120^\circ \pm 5^\circ$	$120^\circ \pm 5^\circ$	$120^\circ \pm 5^\circ$

Table 4 a

ESCA results for the continuous discharge (glow position) of Example 2

COATED SUBSTRATE	glass	Si	PE
carbon atomic %	42.7	42.1	41.5
fluorine atomic %	57.3	57.9	58.5
F/C ratio	1.34	1.37	1.41

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Table 4 b

ESCA results for the continuous discharge (afterglow position) of Example 2

COATED SUBSTRATE	glass	Si	PE
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carbon atomic %	37.1	38.3	38.1
fluorine atomic %	62.9	61.7	61.9
F/C ratio	1.69	1.61	1.62

Table 4 c

ESCA results for the modulated discharge (glow position) of Example 2

COATED SUBSTRATE	glass	Si	PE
carbon atomic %	38.1	39.9	39.2
fluorine atomic %	61.9	60.1	60.8
F/C ratio	1.62	1.51	1.55

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EXAMPLE 3

Three set of substrates of polished silicon, polyethyleneterephthalate (PET), and 3 mm thick FAM (Functional Absorbent Material), an hydrophilic absorbent material made according to the teachings of USP 5 260 345, of areas in the range of 2-10 cm² per substrate, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 1. C₂F₄ was set to feed continuously the reactor at 5 sccm, and the pressure set at 400 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge for 20 min in the modulated mode (10 ms time ON; 190 ms time OFF) with 75 Watt of input power. At the end of the discharge the substrates were extracted from the reactor, and their WCA measured. The values shown in Table 5 were found, which are compared to the WCA values of the unprocessed substrates. A deposition rate of 300 ± 10 Å/min was measured.

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Other substrates were ESCA analysed; their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Table 6. No other elements have been detected (e.g. Si for silicon substrates, and O for PET substrates), thus the coatings can be assumed to

be continuous.

The coated FAM substrate was cut along its thickness, and the freshly cut surface, which was not directly exposed to the discharge, analysed by WCA and ESCA measurements. The data shown in Table 7 demonstrate that the thick FAM sample was treated not only on the surface exposed to the glow, but also inside its bulk, which demonstrates that the plasma treatment is able to penetrate through porous substrates.

Table 5

SUBSTRATE	PET	Si	FAM
WCA unprocessed	$75^{\circ} \pm 3^{\circ}$	$15^{\circ} \pm 3^{\circ}$	WCA unmeasurable, the drop is adsorbed by the material
WCA modulated discharge (glow position)	$155^{\circ} \pm 5^{\circ}$	$155^{\circ} \pm 5^{\circ}$	$155^{\circ} \pm 10^{\circ}$

Table 6

ESCA results for the modulated discharge (glow position) of Example 3

COATED SUBSTRATE	PET	Si	FAM
carbon atomic %	34.8	35.6	34.0
fluorine atomic %	65.2	64.4	66.0
F/C ratio	1.87	1.81	1.94

Table 7

ESCA results for the treated FAM sample of Example 3 cut just after the treatment

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SUBSTRATE	bulk FAM, cut after the treatment
WCA(modulated discharge)	the drop of water is not absorbed the material is evidently much more hydrophobic respect to the untreated one WCA is unmesurable due to surface roughness
carbon atomic %	38.5
fluorine atomic %	61.5
F/C ratio	1.60

As an alternative to provide the substrates of the present invention the method of thin film coating with a monomer followed by surface curing can be used.

- 10 The coating formed by the method of the present invention has a thickness of less than 5 microns, and preferably less than 2 microns and most preferably in the range of 0.001 to 1 microns. The coatings are formed by depositing a vapor of curable monomer, under vacuum, on a movable substrate which is mounted in thermal contact with a support, for continuous processing preferably a rotating
- 15 drum, which is maintained at a temperature below the boiling point of the vaporized monomer under the environmental conditions in vacuum chamber. As a result of this temperature differential, the monomer vapor condenses on the surface of the substrate. The monomer materials utilized in the present invention are relatively low in molecular weight, between 150 and 1000 Atomic Mass Units
- 20 (AMU), and preferably in the range 200 to 300 AMU. Polyfunctional fluoroacrylates and especially fluoroacrylates or mixtures of monofunctional fluoroacrylates and

polyfunctional fluoroacrylates are preferred. The monomers or monomer mixtures employed have an average of about two or more double bonds (i.e., a plurality of olefinic groups) and have a vapor pressure such that they condense on the substrate surface. Such vapor pressures are for example pressure between
5 about $1.33 \cdot 10^{-6}$ mbar and $1.33 \cdot 10^{-1}$ mbar, most preferably a vapor pressure of approximately $1.33 \cdot 10^{-2}$ mbar at standard temperature and pressure, (i.e., relatively low boiling materials) are selected.

These high-vapor-pressure monomers can be flash vaporized already at low
10 temperatures and thus are not degraded (cracked) by the heating process. The absence or low amount of unreactive degradation products results in coatings with a reduced levels of volatile components in which substantially all of the deposited monomer is reactive and will cure to form an integral film when exposed to a source of radiation. These properties make it possible to provide a
15 substantially continuous coating despite the fact that the deposited film is very thin. The cured films exhibit excellent adhesion and are resistant to chemical attack by organic solvents and inorganic salts.

The high speed vacuum coating process for producing water vapour permeable
20 substrates with exceptional water repellent properties on either one side or both sides requires a curable monomer component. Desirably, the curable monomer for obtaining water-repellent coatings comprises fluoro-containing group.

In one embodiment, any suitable fluoromonomer may be used, including, but not limited to, fluoroacrylate monomers, fluoro olefin monomers, fluorostyrene
25 monomers, fluoroalkylene oxide monomers (e.g., perfluoropropylene oxide, perfluorocyclohexene oxide), fluorinated vinyl alkyl ether monomers, and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Fluoromonomers which are polymerized by a free radical polymerization process are preferred.

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In one embodiment, fluorostyrenes and fluorinated vinyl alkyl ether monomers which may be used in the method of the present invention include, but are not

limited to, α -fluorostyrene; β -fluorostyrene; α , β -difluorostyrene; β , β -difluorostyrene; α , β , β -trifluorostyrene; α -trifluoromethylstyrene; 2,4,6-Tris (trifluoromethyl)styrene; 2,3,4,5,6-pentafluorostyrene; 2,3,4,5,6-pentafluoro- α -methylstyrene; and 2,3,4,5,6-pentafluoro- β -methylstyrene.

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In yet another embodiment, tetrafluoroethylene can also be used in the method of the present invention and include, but are not limited to, tetrafluoroethylene-hexafluoropropylene copolymers, tetrafluoroethylene-perfluorovinyl ether copolymers (e.g., copolymers of tetrafluoroethylene with perfluoropropyl vinyl ether), tetrafluoroethylene-ethylene copolymers, and perfluorinated ionomers (e.g., perfluorosulfonate ionomers; perfluorocarboxylate ionomers).

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In still another embodiment, fluorocarbon elastomers (see, e.g., 7 Encyclopedia of Polymer Science & Engineering 257) are a group of fluoro olefin polymers which can also be used in the process of the present invention and include, but are not limited to, poly(vinylidene fluoride-co-hexafluoropropylene); poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene); poly[vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly[tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly(tetrafluoroethylene-co-propylene; and poly(vinylidene fluoride-co-chlorotrifluoroethylene).

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In the preferred embodiment, because of their reactivity, physical properties, and the properties of cured films formed from such components, fluoroacrylates are particularly useful monomeric materials. The term "fluoroacrylate monomer," as used herein, refers to esters of acrylic acid ($H_2C = CHCOOH$) or methacrylic acid ($H_2C = CCH_3 - COOH$), where the esterifying group is a fluorinated group such as perfluoroalkyl. A specific group of fluoroacrylate monomers useful in the method of the invention are compounds represented by formula (I): $H_2C = CR_1 - COO (CH_2)_n R_2$ (I) wherein: n is 1 or 2;

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R_1 is hydrogen or methyl; and R_2 is a perfluorinated aliphatic or perfluorinated aromatic group, such as a perfluorinated linear or branched, saturated or unsaturated C_1 to C_{10} alkyl, phenyl, or naphthyl.

- 5 In a particular embodiment of the invention, R_2 is a C_1 to C_8 perfluoroalkyl or - CH_2 - NR_3 - SO_2 - R_4 , wherein R_3 is C_1 - C_2 alkyl and R_4 is C_1 to C_8 perfluoroalkyl. The term "perfluorinated," as used herein, means that all or essentially all hydrogen atoms on an organic group are replaced with fluorine. Monomers illustrative of Formula (I) above, and their abbreviations, include the following:
- 10 2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");
2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");
2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");
2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");
1,1-Dihydroperfluorooctyl acrylate ("FOA"); and
15 1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

Alternatively, the curable monomer component can also include polyfunctional acrylates, which are set forth in U.S. Patent 4,842,893.

"FOSEA" 5298260